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(56) References: JP 6-220494 (JP, A) JP 11-50097 (JP, A) JP 9-111032 (JP, A) JP 5-140592 (JP, A) JP 5-156292 (JP, A) WO 00/56833 (WO, A1)	

Continued to last page

- (54) [Title of Invention] SOLVENT COMPOSITION FOR CLEANING
- (57) [Scope of Claim]
[Claim 1] A solvent composition for cleaning including:
(a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and
(b) 30 through 70 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitroethane, nitroethane, d-limonene, and

3-methoxybutyl acetate.
[Detailed Description of Invention]

- [0001] [Technical Field to which the Invention Belongs] The present invention relates to a solvent composition for cleaning that contains 1,1,1,3,3-pentafluorobutane as a main ingredient and particularly relates to an art of improving the cleaning ability thereof.
- [0002] [Conventional Art] Conventionally, chlorine-based solvents and fluorine-based solvents have been widely used as, for example, flux cleaners, solvents for dry cleaning, degreasing cleaners, buffing cleaners, resist removing agents, or solvents for removing adhesion water. However, chlorine-based solvents are substances causing groundwater pollution, and fluorine-based solvents are substances causing ozone layer depletion; because of their environmental problems, the use thereof is becoming restricted. Therefore, there is a demand from various fields for a new solvent that would take place of the above-mentioned solvents.
- [0003] 1,1,1,3,3-pentafluorobutane (365mfc, chemical formula: C₄H₉F₅) is one such solvent (see, for example, Japanese Patent Application laid-open Publication No. 5-171189, Japanese Patent Application laid-open Publication No. 5-171190, Japanese Patent Application laid-open Publication No. 6-322394, or Japanese Patent Application laid-open Publication No. 7-188700). 1,1,1,3,3-pentafluorobutane has superior characteristics in that it does not include chlorine in its molecular structure, its ozone depletion potential (ODP) is zero, it is low in toxicity, its global warming potential (GWP) is also small, and thus it is ecological and clean.
- [0004] [Issues to be Addressed by the Invention] However, 1,1,1,3,3-pentafluorobutane (365mfc) has a problem in that its KB value (kauri-butanol value) is approximately 14, which is extremely low, and that it almost has no degreasing ability. If the KB value is low, it will not be possible to exert sufficient cleaning ability required of various kinds of cleaners.
- [0005] Therefore, proposals have been made to increase the cleaning ability by mixing, to 1,1,1,3,3-pentafluorobutane, methylene chloride or 1,1-dichloro-1-fluoroethane (HCFC-141b), which have a higher KB value and degreasing-cleaning ability than the above (see publications Japanese Patent Application laid-open Publication No. 5-171183 and Japanese Patent Application laid-open Publication No. 11-152236).

[0006] However, since methylene chloride is highly toxic, there are concerns about its negative influence on the human body during execution of work. Therefore, use thereof is not only preferable, but it is becoming harder to use. Further, 1,1-dichloro-1-fluoroethane (141b) has a high ozone depletion potential and in the future, it may be restricted under regulations.

[0007] The present invention has been made in view of such circumstances, and an object thereof is to provide a solvent composition for cleaning that contains 1,1,1,3,3-pentafluorobutane as a main ingredient and is superior in cleaning ability, and particularly, in degreasing-cleaning ability.

[0008] [Means for Resolving the Issue] A solvent composition for cleaning according to the present invention for achieving such an object is characterized in including: (a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 30 through 70 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate.

[0009] [0010] [0011] [0012] [0013] [0014] [0015] [0016] Nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate are such solvents found by the present inventor as to be suitable for increasing the cleaning ability of 1,1,1,3,3-pentafluorobutane. These have sufficient degreasing-cleaning abilities.

[0017] 1,1,1,3,3-pentafluorobutane is set to 30 through 70 wt%, and one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate is set to 30 through 70 wt% because, if the content of the latter is too small, the increase in the cleaning ability is not so sufficient, and thus it is not possible to obtain a sufficient cleaning effect, whereas if the content of the latter is too large, the characteristics of nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate will become too significant, and it will not be possible to take full advantage of the superior features of 1,1,1,3,3-pentafluorobutane.

[0018]

[Embodiment of the Invention] An embodiment of a solvent composition for cleaning according to the present invention will be described below. The solvent composition for cleaning according to the present invention includes: (a) 30 through 70 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 30 through 70 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate. Other than this, it is possible to achieve compositions that are superior in cleaning ability, as with the present invention, with the following two types of solvent compositions for cleaning.

[0019] [1] A solvent composition including: (a) 30 through 80 wt% of 1,1,1,3,3-pentafluorobutane; and (b) 20 through 70 wt% of normal propyl bromide and/or isopropyl bromide.

[0020] [2] A solvent composition including: (a) 27 through 80 wt% of 1,1,1,3,3-pentafluorobutane; (b) 20 through 70 wt% of normal propyl bromide and/or isopropyl bromide; and (c) 3 through 15 wt% of one kind of solvent or a mixed solvent including at least two kinds of solvents selected from among alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols.

[0021]

[0022] Normal propyl bromide (synonym: n-propyl bromide; 1-bromopropane, referred to simply as NPB below) and isopropyl bromide (synonym: isopropyl bromide; 2-bromopropane, referred to simply as IPB below) have been found to be solvents that are suitable for increasing the cleaning ability of 1,1,1,3,3-pentafluorobutane. NPB and IPB have a relatively high KB value of 123 and are superior in degreasing and cleaning. Further, as with 1,1,1,3,3-pentafluorobutane, they are nonflammable and have incombustible or flame-resistant characteristics and are therefore not classified as hazardous materials and are safe and easy to handle, and they have superior characteristics in that they do not include chlorine or fluorine in their molecular structures, their ozone depletion potential (ODP) and their global warming potential (GWP) are also small, and thus they are ecological and clean. By mixing NPB and/or IPB, which are high in KB value, to 1,1,1,3,3-pentafluorobutane, it is possible to achieve a significant increase in cleaning ability, and particularly, degreasing-cleaning ability, and thus, it is possible for the solvent to exhibit sufficient performance as various types of cleaners. Further, as with

conventional cases, it is nonflammable and thus is not classified as hazardous material and is safe and easy to handle. Further, its ozone depletion potential (ODP) and global warming potential (GWP) are also small, and thus, it is ecological and clean. 1,1,1,3,3-pentafluorobutane is set to 30 through 80 wt% and NPB and/or IPB is set to 20 through 70 wt% because if the content of NPB and/or IPB is too small, then the cleaning ability will not be increased that much and a sufficient cleaning effect cannot be obtained. Further, if the content of NPB and/or IPB is too large, then the characteristics of NPB and/or IPB will become too significant and dissolvability will become too large, and it will not be possible to take full advantage of the superior features of 1,1,1,3,3-pentafluorobutane. By ensuring at least 30 wt% in content of 1,1,1,3,3-pentafluorobutane, its characteristics can be exhibited. Further, at least one kind of solvent selected from alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols is mixed in order to reduce the content of 1,1,1,3,3-pentafluorobutane, and ② to dissolve water-soluble inorganic substances etc. contained in flux etc. that cannot be sufficiently dissolved by normal propyl bromide and/or isopropyl bromide. 1,1,1,3,3-pentafluorobutane is extremely expensive and may give rise to a significant increase in cost if it is used in large quantities, and therefore, by mixing the solvents described above, which are much inexpensive, as a substitute, it is possible to avoid a significant increase in cost. The content of these solvents is set to 3 wt% or more in order to sufficiently dissolve the water-soluble inorganic substances etc. contained in flux etc. Further, the content of these solvents is set to 15 wt% or less because if too much of these solvents are mixed, the solvent composition will be turned into a combustible since these solvents are flammable and are classified as hazardous materials. As regards normal propyl bromide (NPB) and isopropyl bromide (IPB), either one may be blended individually, or both may be blended. Further, since NPB and IPB are likely to cause metal reaction with aluminum, its alloys, etc., it is preferable to add a slight amount or a small amount of at least one kind of substance selected from a group consisting of nitroalkanes, ethers, epoxides, and amines as a stabilizer for preventing such a reaction. Further, in the present cleaning solvent, it is preferable to add a slight amount or a small amount of perfume such as d-limonene to control the odor of NPB.

[0023] Similarly, as for 1,1,1,3,3-pentafluorobutane, if the object to be cleaned is made of iron, zinc, aluminum, copper,

brass, etc. when it is used for cleaning in a heated state or as steam, there are cases in which it becomes unstable because of an influence caused by the metal. Therefore, it is preferable to add, as a stabilizer, at least one kind of compound selected from nitro compounds, phenols, amines, ethers, amylenes, epoxides, or triazoles. Specifically, as stabilizers, there are: epoxides such as propylene oxide; 1,2-butylene oxide, and glycidol; phosphites such as dimethyl phosphite, diisopropyl phosphite, and diphenyl phosphite; thiophosphites such as triallyl trichlorophosphite; phosphine sulphides such as triphenoxyposphine sulphide and trimethylphosphine sulphide; boron compounds such as boric acid, triethyl borate, triphenyl borate, phenylboronic acid, and diphenylboronic acid; phenols such as 2,6-di-tert-butyl-para-cresol; nitroalkanes such as nitromethane and nitroethane; acrylic esters such as methyl acrylate and ethyl acrylate; and also, dioxane, tert-butanol, pentaerythritol, and para-isopropenyl toluene. As for the amount of addition of these stabilizers, it is preferable to set the amount to 0.01 through 5 wt% of the whole amount of the solvent composition for cleaning, although the amount is not to be particularly limited.

[0024] On the other hand, it is possible to list, for example, the following as alkanes with a carbon number of 5 or more and cycloalkanes with a carbon number of 5 or more, but they are not limited to these: pentane, 2-methyl butane, 2,2-dimethyl propane, hexane, 2-methyl pentane, 3-methyl pentane, 2,2-dimethyl butane, 2,3-dimethyl butane, heptane, 2-methyl hexane, 3-methyl hexane, 2,3-dimethyl pentane, 2,4-dimethyl pentane, octane, 2,2,3-trimethyl pentane, 2,2,4-trimethyl pentane, cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclohexane, and ethyl cyclohexane. Further, alcohols include, for example: methanol, ethanol, i-propanol, n-propanol, n-butanol, i-butanol, s-butanol, and t-butanol. As regards the alkanes with a carbon number of 5 or more, the cycloalkanes with a carbon number of 5, and the alcohols, one kind of solvent may be mixed, or a mixed solvent containing two kinds or more of them may be mixed.

[0025] Furthermore, as regards nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate, at least one kind of solvent selected from the above may be mixed, and it is also needless to say that two kinds or more of the above may be mixed.

[0026] As main applications of the solvent composition for cleaning according to the present invention, it is possible to name: resist removing agents, flux cleaners, degreasing cleaners for oils and fats etc., buffing cleaners, solvents for

dry cleaning, removing agents for grease, oil, wax, ink etc., solvents for paint, extractants, cleaners for various articles made of glass, ceramics, rubber, metal etc. and particularly for IC parts, electrical equipments, precision equipments, optical lenses, etc., or water removing agents.

Further, as for the cleaning method to which the solvent composition for cleaning according to the present invention can be applied, there are, for example, manual wiping, immersion, spraying, shaking, ultrasonic cleaning, and steam cleaning.

Next, various tests that were carried out for confirming the performance of the solvent composition for cleaning according to the present invention are described below.

<< Machine Oil Cleaning Test >> In this test, test pieces made of SUS-304 (length 25 mm x width 30 mm x thickness 2 mm) were prepared, and, after immersing these test pieces into machine oil (CQ-30: made by Nippon Oil Co., Ltd.), they were immersed into each cleaning fluid for approximately 3 minutes. After subjecting the test pieces to a drying process, the cleansing state of the test pieces was studied. Cleaning fluids obtained by mixing each of normal propyl bromide (NPB), isopropyl bromide (IPB), nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 1,1,1,3,3-pentafluorobutane (365mfc) were used. The following table 1 through table 3 summarize the composition of each cleaning fluid and the results of cleaning. It should be noted that a small amount of nitroethane is mixed, as a stabilizer, to the cleaning fluid to which normal propyl bromide (NPB) or isopropyl bromide (IPB) is mixed.

[0030]

[Table 1]

Machine Oil Cleaning Test 1 (365mfc - NPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	85	80	75	70	65	60	50	40
NPB (wt%)	0	10	15	20	25	30	35	40	50	60
Cleaning results	x	x	x	O	O	⊙	⊙	⊙	⊙	⊙

X: small cleaning effect O: satisfactory ⊙: extremely good

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

NPB: normal propyl bromide

[Table 2]

Machine Oil Cleaning Test 2 (365mfc - IPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	85	80	75	70	65	60	50	40
IPB (wt%)	0	10	15	20	25	30	35	40	50	60
Cleaning results	x	x	x	O	O	⊙	⊙	⊙	⊙	⊙

X: small cleaning effect O: satisfactory ⊙: extremely good

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

IPB: isopropyl bromide

[Table 3]

Machine Oil Cleaning Test 3

(365mfc, nitroethane, nitromethane, d-limonene)

	365mfc (wt%)	nitroethane (wt%)	nitromethane (wt%)	d-limonene (wt%)	3-MBA (wt%)	Cleaning ability
A	80	20	—	—	—	x
B	75	25	—	—	—	x
C	70	30	—	—	—	O
D	65	35	—	—	—	O
E	60	40	—	—	—	O
F	50	50	—	—	—	O
G	80	—	20	—	—	x
H	75	—	25	—	—	x
I	70	—	30	—	—	O
J	65	—	35	—	—	O
K	60	—	40	—	—	O
L	50	—	50	—	—	O
M	80	—	—	20	—	x
N	75	—	—	25	—	x
O	70	—	—	30	—	O
P	65	—	—	35	—	O
Q	60	—	—	40	—	O
R	50	—	—	50	—	O
S	80	—	—	—	20	x
T	75	—	—	—	25	x
U	70	—	—	—	30	O
V	65	—	—	—	35	O
W	60	—	—	—	40	O
Y	50	—	—	—	50	O

O: satisfactory X: small cleaning effect

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)

3-MBA: 3-methoxybutyl acetate

[0031] From these test results, it has been found that, in terms of cleaning machine oil, it is necessary to include, with respect to 1,1,1,3,3-pentafluorobutane (365mfc), 20 wt% or more of normal propyl bromide or isopropyl bromide, and 30 wt% or more of nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate.

[0032] << Flux Cleaning Test >> In this test, flux (TAMURA P-AL-4 made by TAMURA corporation) was applied to the whole surface of a printed wiring board for testing, and, after subjecting it to a burning process in an electric furnace at approximately 200 °C for approximately 2 minutes, it was immersed into a cleaning fluid for approximately 3 minutes. Then, after subjecting the printed wiring board to a drying process, the cleansing state was examined. Cleaning fluids obtained by mixing each of normal propyl bromide (NPB), isopropyl bromide (IPB), nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 1,1,1,3,3-pentafluorobutane (365mfc) were used. The following table 4 through table 6 summarize the composition of each cleaning fluid and the results of cleaning. It should be noted that a small amount of nitroethane is mixed, as a stabilizer, to the cleaning fluid to which normal propyl bromide (NPB) or isopropyl bromide (IPB) is mixed.

[0033]

[Table 4]

Flux Cleaning Test 1 (365mfc - NPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	80	70	65	60	55	50	40	30
NPB (wt%)	0	10	20	30	35	40	45	50	60	70
Cleaning results	x	x	x	x	O	⊙	⊙	⊙	⊙	⊙

x: small cleaning effect O: satisfactory ⊙: extremely good
365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)
NPB: normal propyl bromide

[Table 5]

Flux Cleaning Test 2 (365mfc - IPB)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	100	90	80	70	65	60	55	50	40	30

IPB (wt%)	0	10	20	30	35	40	45	50	60	70
Cleaning results	x	x	x	x	O	⊙	⊙	⊙	⊙	⊙

x: small cleaning effect O: satisfactory ⊙: extremely good
365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₉F₅)
IPB: isopropyl bromide

[Table 6]

Flux Cleaning Test 3

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt%)	nitroethane (wt%)	nitromethane (wt%)	d-limonene (wt%)	3-MBA (wt%)	Cleaning ability
A	80	20	—	—	—	x
C	70	30	—	—	—	x
D	65	35	—	—	—	x
E	60	40	—	—	—	O
F	50	50	—	—	—	O
G	40	60	—	—	—	O
H	30	70	—	—	—	O
I	20	80	—	—	—	O
J	80	—	20	—	—	x
K	70	—	30	—	—	x
L	65	—	35	—	—	x
M	60	—	40	—	—	O
N	50	—	50	—	—	O
O	40	—	60	—	—	O
P	30	—	70	—	—	O
Q	20	—	80	—	—	O
R	80	—	—	20	—	x
S	70	—	—	30	—	x
T	65	—	—	35	—	x
U	60	—	—	40	—	O
V	50	—	—	50	—	O
W	40	—	—	60	—	O
X	30	—	—	70	—	O
Y	20	—	—	80	—	O
Z	10	—	—	90	—	O
	5	—	—	95	—	O
AA	80	—	—	—	20	x
AB	70	—	—	—	30	x
AC	65	—	—	—	35	x
AD	60	—	—	—	40	O
AE	50	—	—	—	50	O

AF	40	—	—	—	60	○
AG	30	—	—	—	70	○
AH	20	—	—	—	80	○
AI	10	—	—	—	90	○

Q:	satisfactory	X: small cleaning effect
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365mfc: 1,1,1,3,3-pentafluorobutane ($C_4H_2F_5$)

3-MBA: 3-methoxybutyl acetate

[0034] From these test results, it has been found that, in terms of cleaning flux, it is necessary to include, with respect to 1,1,1,3,3-pentafluorobutane (365mfc), 35 wt% or more of normal propyl bromide (NPB) or isopropyl bromide (IPB), and 40 wt% or more of nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate (3-MBA).

[0035] << Influence on Plastics, Rubbers, Etc. >>
Tests for examining the influence of the solvent on various kinds of plastics, rubbers, etc. were carried out. In these tests, soft vinyl chloride, hard vinyl chloride, polycarbonate (PC), acrylic resin, nylon 66 (registered trademark), polyacetal, polyurethane resin, phenolic resin, epoxy resin, melamine resin, urea resin, polyethylene, and polypropylene were prepared as the plastics, fluoro rubber, chloroprene rubber, silicone rubber, urethane rubber, SAR, natural rubber, and butyl rubber were prepared as the rubbers, and a test of immersing each of them into the cleaning fluid for approximately 6 hours at room temperature was carried out. Then, a drying process was performed and the presence or absence of influence was studied.

[0036]

[Table 7]

Influence on Plastics, Rubbers, Etc. 1 (365mc, NPB, IPB)

[illegible]

11

[illegible]

○ : no influence X : having influence

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₅F₅)

363ME: 1,1,1,3,3-pentachloro-
NPH: normal propyl bromide

epfwmqd yadordobf : bdl
epfwmqd yadordobf : bdl

[Table 8]

Influence on Plastics, Rubbers, Etc. 2

(365m μ . nitroethane, nitromethane)

(365mfc, nitroethane, nitromethane)										
	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	70	60	50		30	70	60	50	40	30
nitroethane (wt%)	30	40	50	60	70	—	—	—	—	—
nitromethane (wt%)	—	—	—	—	—	30	40	50	60	70
vinyl chloride (soft)	○	○	○	x	x	○	○	x	x	x
vinyl chloride (hard)	○	○	○	x	x	○	○	x	x	x
polycarbonate	○	○	○	x	x	○	○	x	x	x
acrylic resin	○	○	○	○	○	○	○	○	○	○
nylon 88	○	○	○	○	○	○	○	○	○	○
polyacetal	○	○	○	○	○	○	○	○	○	○
polyurethane resin	○	○	○	○	○	○	○	○	○	○
phenolic resin	○	○	○	○	○	○	○	○	○	○
epoxy resin	○	○	○	○	○	○	○	○	○	○
melamine resin	○	○	○	○	○	○	○	○	○	○
urea resin	○	○	○	○	○	○	○	○	○	○
polyethylene	○	○	○	○	○	○	○	○	○	○
polypropylene	○	○	○	○	○	○	○	○	○	○
fluoro rubber	○	○	○	○	○	○	○	○	○	○
chloroprene rubber	○	○	○	x	x	○	○	○	x	○
silicone rubber	○	○	○	○	○	○	○	○	○	○
urethane rubber	○	○	○	○	○	○	○	○	x	x
SBR	○	○	○	○	○	○	○	○	x	x
natural rubber	○	○	○	x	x	○	○	○	x	x
butyl rubber	○	○	○	x	x	○	○	○	x	x

O : no influence	X : having influence
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365mg; 1,1,1,3,3-pentafluorobutane (C₄H₂F₅)

[Table 9]

12

Influence on Plastics, Rubbers, Etc. 3
(365mfc, d-limonene, 3-MBA)

	A	B	C	D	E	F	G	H	I	J
365mfc (wt%)	70	60	50	40	30	70	60	50	40	30
d-limonene (wt%)	30	40	50	60	70	—	—	—	—	—
3-MBA (wt%)	—	—	—	—	—	30	40	50	60	70
vinyl chloride (soft)	O	O	O	X	X	O	O	X	X	X
vinyl chloride (hard)	O	O	O	X	X	O	O	X	X	X
polycarbonate	O	O	O	O	O	O	O	O	O	O
acrylic resin	O	O	O	O	O	O	O	O	O	O
nylon 88	O	O	O	O	O	O	O	O	O	O
polyacetal	O	O	O	O	O	O	O	O	O	O
polyurethane resin	O	O	O	O	O	O	O	O	O	O
phenolic resin	O	O	O	O	O	O	O	O	O	O
epoxy resin	O	O	O	O	O	O	O	O	O	O
melamine resin	O	O	O	O	O	O	O	O	O	O
urea resin	O	O	O	O	O	O	O	O	O	O
polyethylene	O	O	O	O	O	O	O	O	O	O
polypropylene	O	O	O	O	O	O	O	O	O	O
fluoro rubber	O	O	O	O	O	O	O	O	O	O
chloroprene rubber	O	O	O	X	X	O	O	O	X	X
silicone rubber	O	O	O	O	O	O	O	O	O	O
urethane rubber	O	O	O	O	X	O	O	O	X	X
SBR	O	O	O	X	X	O	O	O	X	X
natural rubber	O	O	O	X	X	O	O	O	X	X
butyl rubber	O	O	O	O	X	O	O	O	O	X

O : no influence X : having influence

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₃F₅)

3-MBA: 3-methoxybutyl acetate

[0037] From these results, it was possible to confirm that in some cases, soft and hard vinyl chloride and polycarbonate are negatively affected. It was found that, if negative influence is to be kept from being exerted on soft vinyl chloride, hard vinyl chloride, and polycarbonate, then it is necessary to set the content of normal propyl bromide and isopropyl bromide to 45 wt% or less, and set the content of nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) to 50 wt% or less, with respect to 1,1,1,3,3-pentafluorobutane (365mfc).

<< Flammability Test >> In this test, a study was made on the relationship between flammability and the content for when 1,1,1,3,3-pentafluorobutane (365mfc) includes alkanes with a carbon number of 3 or more, cycloalkanes with a carbon number of 3 or more, or alcohols, because these solvents

have flammability and are combustibles. Ethyl alcohol (ethanol), methyl alcohol (methanol), and heptane were used as the solvents to be mixed. The following table 10 summarizes the test results. It should be noted that the flammability was studied according to the tag closed cup method.

[0039]

[Table 10]

Flammability Test 1

(365mfc, NPB, ethanol, methanol, heptane)

	365mfc (wt %)	NPB (wt %)	ethanol (wt %)	methanol (wt %)	heptane (wt %)	flamma- bility
A	80	20	0	—	—	no
B	77	20	3	—	—	no
C	75	20	5	—	—	no
D	72	20	8	—	—	no
E	70	20	10	—	—	no
F	67	20	13	—	—	no
G	66	20	15	—	—	no
H	62	20	18	—	—	yes
I	60	20	20	—	—	yes
J	77	20	—	3	—	no
K	75	20	—	5	—	no
L	72	20	—	8	—	no
M	70	20	—	10	—	no
N	67	20	—	13	—	no
O	65	20	—	15	—	no
P	62	20	—	18	—	yes
Q	60	20	—	20	—	yes
R	77	20	—	—	3	no
S	75	20	—	—	5	no
T	72	20	—	—	8	no
U	70	20	—	—	10	no
V	67	20	—	—	13	no
W	65	20	—	—	15	no
X	62	20	—	—	18	yes
Y	60	20	—	—	20	yes

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₃F₅)

NPB: normal propyl bromide

[0040] From these results, it was found that, since flammability arises when 18 wt% or more of each solvent of ethyl alcohol, methyl alcohol, and heptane is contained, in order to keep the solvent composition for cleaning (type 2) according to the present invention from becoming flammable, it is

necessary to set the content of these solvents to 15 wt% or less. [0041] Further, since nitromethane, nitroethane, d-limonene, and 3-methoxybutyl acetate (3-MBA) similarly have flammability, the relationship between flammability and the content of these solvents was also studied. The following table 11 summarizes the test results. It should be noted that the flammability was measured according to the Tag closed cup method.

[0042]

[Table 11]

Flammability Test 2

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt %)	nitroethane (wt %)	nitromethane (wt %)	d-limonene (wt %)	3-MBA (wt %)	flamma- bility
A	70	30	—	—	—	no
B	60	40	—	—	—	no
C	50	50	—	—	—	no
D	40	60	—	—	—	no
E	30	70	—	—	—	no
F	20	80	—	—	—	yes
G	10	90	—	—	—	yes
H	70	—	30	—	—	no
I	60	—	40	—	—	no
J	50	—	50	—	—	no
K	40	—	60	—	—	no
L	30	—	70	—	—	no
M	20	—	80	—	—	no
N	10	—	90	—	—	yes
O	70	—	—	30	—	no
P	60	—	—	40	—	no
Q	50	—	—	50	—	no
R	40	—	—	60	—	no
S	30	—	—	70	—	no
T	20	—	—	80	—	no
U	10	—	—	90	—	no
V	5	—	—	95	—	yes
W	70	—	—	—	30	no
Y	60	—	—	—	40	no
Z	50	—	—	—	50	no
AA	40	—	—	—	60	no
AB	30	—	—	—	70	no
AC	20	—	—	—	80	no
AD	10	—	—	—	90	no
AE	5	—	—	—	95	yes

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₂F₅)
3-MBA: 3-methoxybutyl acetate

[0043] From these results, it was found that, since flammability arises when 80 wt% or more of nitromethane or nitroethane is contained, and 95 wt% or more of d-limonene or 3-methoxybutyl acetate (3-MBA) is contained, in order to keep the solvent composition for cleaning (type 3) according to the present invention from becoming flammable, it is necessary to set the content of nitromethane and nitroethane to 70 wt% or less, and the content of d-limonene and 3-methoxybutyl acetate (3-MBA) to 90 wt% or less.

[0044] << Metal Corrosion Test >> In this test, according to JIS-K1600, aluminum pieces (JIS-H-4000, Al100P) were arranged in both the liquid phase portion and the gas phase portion of the cleaning fluid after cleaning, and the state of corrosion of metal after approximately 48 hours was studied.

[0045]

[Table 12]

Metal Corrosion Test 1 (365mfc, NPB, IPB)

	A	B	C	D	E	F	G	H	I	J	K	L
365mfc (wt%)	80	70	60	50	40	30	80	70	60	50	40	30
NPB (wt%)	20	30	40	50	60	70	—	—	—	—	—	—
IPB (wt%)	—	—	—	—	—	—	20	30	40	50	60	70
results	O	O	O	O	O	O	O	O	O	O	O	O

X : corrosion O : no corrosion

365mfc: 1,1,1,3,3-pentafluorobutane (C₄H₂F₅)

NPB: normal propyl bromide

IPB: isopropyl bromide

[Table 13]

Metal Corrosion Test 2

(365mfc, nitroethane, nitromethane, d-limonene, 3-MBA)

	365mfc (wt %)	nitroethane (wt %)	nitromethane (wt %)	d-limonene (wt %)	3-MBA (wt %)	results
A	70	30	—	—	—	O
B	60	40	—	—	—	O
C	50	50	—	—	—	O
D	40	60	—	—	—	O

contains 1,1,1,3,3-pentafluorobutane as a main ingredient and that is superior in cleaning ability. [Means for Resolution] Normal propyl bromide, isopropyl bromide, nitromethane, nitroethane, d-limonene, or 3-methoxybutyl acetate is mixed to 1,1,1,3,3-pentafluorobutane. Further, to the above, at least one kind of solvent selected from among alkanes with a carbon number of 5 or more, cycloalkanes with a carbon number of 5 or more, or alcohols is mixed.

Continued from Front Page

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REGISTRY (STN)

また、炭素と同じく引火性がないから危険物に該当す。安全で取り扱いやすい。また、オゾン破壊係数 (ODP) 及び温暖化係数 (GWP) も小さく、環境に優しいクリンである。1, 1, 1, 3, 3-ペンタフルオロブタンを30~80重量%、NPB及び/又はIPBを20~70重量%に調整したものは、NPB及び/又はIPBの含有量が少なすぎると、あまり洗淨能力が向上せず、十分な洗淨効果を得ることができないからである。また、NPB及び/又はIPBの含有量が多すぎると、多すぎると、NPB及び/又はIPBの毒性が大きくなり、溶解力も向上し過ぎしまい、1, 1, 1, 3, 3-ペンタフルオロブタンの優れた特性が生かし切れなくなるからである。1, 1, 1, 3, 3-ペンタフルオロブタンの含有量を少なくとも30重量%調整すること、その毒性を軽減させることが可能である。また、炭素6個以上のアルカン類、炭素数5個以上のシクロアルカン類、アルコール類から選ばれる少なくとも1種の溶剤を配合するものは、0, 1, 1, 1, 3, 3-ペンタフルオロブタンの含有量を少なくするとともに、0, 1, 1, 1, 3, 3-ペンタフルオロブタン及び/又はIPBの含有量を30重量%以上としたものである。これらの溶剤の含有量を30重量%以上としたのは、フラスコ等に含まれる水可溶性のある炭水化物等を十分に溶解するためである。また、これらの溶剤の含有量を30重量%以下としたのは、これらの溶剤の引火性を有し危険物に該当するために、あまり大量に配合すると可燃物となるためである。ここで、ノルマルプロピルフロマイド (NPB) 及びイソプロピルフロマイド (IPB) についてはどちらから一方が単独で配合されてもよく、また混合が配合されてもよい。また、NPB及びIPBについては、アルミニウムまたはその合金等と金属反応し易いことから、この反応を防止するためにニトロアルカン類、エーテル類、エポキシド類およびアミン類の群から選ばれる少なくとも1種の物質が安定剤として微量または少量添加されるとよい。また、本洗淨用溶剤にあっては、NPBの臭気を抑制するために、d-リモネン等をはじめてとす香料が微量または少量添加されるとよい。

【0026】本発明に係る洗淨用溶剤組成物の主な用途としては、レジスト剥離剤、フラックス洗淨剤・油脂剤等の脱脂洗淨剤、バフ研削洗淨剤、ドライクリーニング剤、グリース・油・ワックス・インキ等の除去剤、塗料用溶剤、抽出剤、ガラス・セラミックス・ゴム・金属製各種物品、特にIC部品、電気機器、精密機器、光学レンズ等の洗淨剤や水切り剤等を挙げることができ、る。

【0027】また、本発明に係る洗淨用溶剤組成物が適

用可能な洗淨方法としては、手拭き、スプレー、拭取、超音波洗淨、蒸気洗淨等がある。

【0028】次に本発明に係る洗淨用溶剤組成物の性質を説明する。

【0029】《炭化水素洗淨剤》この洗淨剤は、SUS-304のテストピース (縦25mm×横30mm×厚2mm) を用意し、このテストピースを炭化水素洗淨剤 (30:日本石油株式会社製) 中に浸漬した後、各洗淨剤中から3分間区渡し、その後テストピースを乾燥処理してからテストピースの洗淨具合を調べた。洗淨剤として、1, 1, 1, 3, 3-ペンタフルオロブタン (365mole-NPB) は、1, 1, 1, 3, 3-ペンタフルオロブタン (365mole-NPB) 炭化水素洗淨剤1 (365mole-NPB)

は、1, 1, 1, 3, 3-ペンタフルオロブタン (365mole-NPB) 炭化水素洗淨剤1 (365mole-NPB)

	A	B	C	D	E	F	G	H	I	J
365mole (重量%)	100	90	85	80	75	70	65	60	50	40
NPB (重量%)	0	10	15	20	25	30	35	40	50	60
洗淨結果	×	×	×	×	○	◎	◎	◎	◎	◎

×: 洗淨効果減少 ○: 良好 ◎: 非常に良好
365mole: 1, 1, 1, 3, 3-ペンタフルオロブタン (C₄H₉F₅)
NPB: ノルマルプロピルフロマイド

炭化水素洗淨剤2 (365mole-NPB)

	A	B	C	D	E	F	G	H	I	J
365mole (重量%)	100	90	85	80	75	70	65	60	50	40
IPB (重量%)	0	10	15	20	25	30	35	40	50	60
洗淨結果	×	×	×	×	○	◎	◎	◎	◎	◎

×: 洗淨効果減少 ○: 良好 ◎: 非常に良好
365mole: 1, 1, 1, 3, 3-ペンタフルオロブタン (C₄H₉F₅)
IPB: イソプロピルフロマイド

【表2】

【表3】

アクリル樹脂、ナイロン66（登録商標）、ポリアセタール、ポリウレタン樹脂、フェノール樹脂、エポキシ樹脂、メラミン樹脂、ユリア樹脂、ポリエチレン、ポリブチレン、ポリプロピレン、ポリスチレン、ポリオレフィン、天然ゴム、ブチルゴムを用い、それぞれ常温にて約8時間乾燥後に厚漬するテストを行った。その後、乾燥処理を行って影響の有無を調べた。

ノール)、ヘプタンを使用した。試験結果を次の表10にまとめた。なお、引火性はタグ密閉方式により調べた。

引火性試験1(365mfa, NPB, エタノール, メタノール, ヘプタン)

	365mfa (質量%)	NPB (質量%)	エタノール (質量%)	メタノール (質量%)	ヘプタン (質量%)	引火性
A	80	20	0	—	—	燃
B	77	20	3	—	—	燃
C	75	20	5	—	—	燃
D	72	20	8	—	—	燃
E	70	20	10	—	—	燃
F	67	20	13	—	—	燃
G	65	20	16	—	—	燃
H	62	20	18	—	—	燃
I	60	20	20	—	—	燃
J	77	20	—	3	—	燃
K	75	20	—	5	—	燃
L	72	20	—	8	—	燃
M	70	20	—	10	—	燃
N	67	20	—	13	—	燃
O	65	20	—	16	—	燃
P	62	20	—	18	—	燃
Q	60	20	—	20	—	燃
R	77	20	—	—	3	燃
S	75	20	—	—	5	燃
T	72	20	—	—	8	燃
U	70	20	—	—	10	燃
V	67	20	—	—	13	燃
W	65	20	—	—	16	燃
X	62	20	—	—	18	燃
Y	60	20	—	—	20	燃

365mfa:1, 1, 1, 3, 3-ペンタフルオロブタン(C₄H₉F₅)
NPB:ノルマルプロピルブロマイド

[0040] この結果から、エチルアルコール、メチルアルコール及びヘプタンの各溶剤ともに18重量%以上含有すると引火性を持つようになっていることから、本発明に係る洗淨用溶剤組成物(タイプA)において引火性を持たないようには、これらの溶剤の含有量を18重量%以下に設定する必要があることがわかった。

[0041] また、ニトロメタン、ニトロエタン、d-

リモネン及び3-メトキシ・ブチルアセテート(3-MBA)についても同様に引火性があることから、これらの溶剤についても含有量と引火性との関係について調べた。試験結果を次の表11にまとめた。なお、引火性はタグ密閉方式により測定した。

[0042]
[表11]

[0043] この結果から、ニトロメタン及びニトロエタンについては80重量%以上、またd-リモネン及び3-メトキシ・ブチルアセテート(3-MBA)については85重量%以上でそれぞれ引火性を持つようになっているから、本発明に係る洗淨用溶剤組成物(タイプB)において引火性を持たないようにはニトロメタン及びニトロエタンの含有量を70重量%以下に、またd-リモネン及び3-メトキシ・ブチルアセテート(3-MBA)の含有量を90重量%以下に設定する必要があることがわかった。

金沢商標1(365mfa-NPB:IPB)

	A	B	C	D	E	F	G	H	I	J	K	L
365mfa(質量%)	80	70	60	50	40	30	80	70	60	50	40	30
NPB(質量%)	20	30	40	50	60	70	—	—	—	—	—	—
IPB(質量%)	—	—	—	—	—	—	20	30	40	50	60	70
総量	0	0	0	0	0	0	0	0	0	0	0	0

*: 腐食有り O: 腐食無し
365mfa:1, 1, 1, 3, 3-ペンタフルオロブタン(C₄H₉F₅)
NPB:ノルマルプロピルブロマイド
IPB:イソプロピルブロマイド

[表13]

引火性試験2(365mfa, ニトロエタン, ニトロメタン, d-リモネン, 3-MBA)

	365mfa (質量%)	ニトロエタン (質量%)	ニトロメタン (質量%)	d-リモネン (質量%)	3-MBA (質量%)	引火性
A	70	30	—	—	—	燃
B	60	40	—	—	—	燃
C	50	50	—	—	—	燃
D	40	60	—	—	—	燃
E	30	70	—	—	—	燃
F	20	80	—	—	—	燃
G	10	90	—	—	—	燃
H	70	—	30	—	—	燃
I	60	—	40	—	—	燃
J	50	—	50	—	—	燃
K	40	—	60	—	—	燃
L	30	—	70	—	—	燃
M	20	—	80	—	—	燃
N	10	—	90	—	—	燃
O	70	—	—	30	—	燃
P	60	—	—	40	—	燃
Q	50	—	—	50	—	燃
R	40	—	—	60	—	燃
S	30	—	—	70	—	燃
T	20	—	—	80	—	燃
U	10	—	—	90	—	燃
V	70	—	—	—	30	燃
W	60	—	—	—	40	燃
X	50	—	—	—	50	燃
Y	40	—	—	—	60	燃
AA	30	—	—	—	70	燃
AB	20	—	—	—	80	燃
AC	10	—	—	—	90	燃
AD	70	—	—	—	—	燃
AE	60	—	—	—	—	燃

365mfa:1, 1, 1, 3, 3-ペンタフルオロブタン(C₄H₉F₅)
3-MBA:3-メトキシ・ブチルアセテート

[0044] 《金属腐食試験》 この試験では、JIS-K1600に準じて、洗浄後の洗浄液の液相部および相部の各々にアルミニウム片(JIS-H-4000, A1100P)を配置し、約48時間後の金属の腐食状況を調べた。

[0045]
[表12]

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